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CHARGE TRANSFER COMPLEXES OF CERTAIN AROMATIC POLYIMIDES

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16. Abstract By electron spectroscopy it was shown that aromatic polyimides containing electron-donor residues of diamines $-C_6H_4-X-C_6H_4-$ (X=NH, NCH_3, NC_6H_5, O, S, and CH_2) form charge transfer complexes with low-molecular-weight electron acceptors. Based on the data obtained, the hypothesis was advanced that the coloration of the polyimides per se is due to the formation of charge transfer complexes between the electron-acceptor imide fragments and the electron-donor residues of the diamines.

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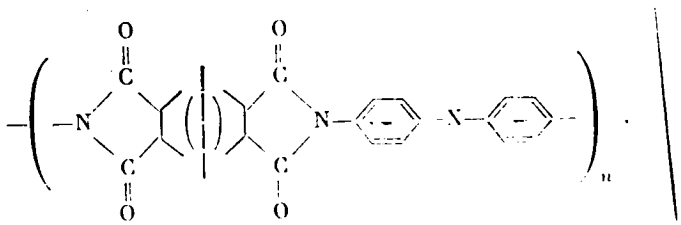
CHARGE TRANSFER COMPLEXES OF CERTAIN AROMATIC POLYIMIDES

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Charge transfer complexes of polymers containing electron donor or electron acceptor groups are at present an interesting subject of investigation owing to the elucidation of the electroconductivity mechanism of polymers [1-3]. /378*

In this article, charge transfer complexes of aromatic polyimides with the general structure



were investigated by electron spectroscopy, where X = NH, NCH_3, NC_6H_5, S, O, and CH_2, with the following low-molecular-weight electron acceptors: p-chloranil, o- and p-bromanils, 2,3-dichlor-5,6-dicyanbenzoquinone (DCDC), 7,7',8,8'-tetracyanquinodimethane (TCQM), and tetracyanethylene (TCE).

The polyimides were prepared by the usual two-stage method [4,5]; as the starting products, use was made of pyromellitic acid dianhydride (PDA), the dianhydrides of 3,4,3',4'-diphenoxidetetracarboxylic (DODA), 3,4,3',4'-diphenylsulfonetetracarboxylic DSDA), and 3,4,3',4'-benzophenonetetracarboxylic (BPDA) acids. The acceptor additives were introduced into solutions of the corresponding polyamidoacids (PAA) in N,N-dimethylacetamide, from which films were /379

*Numbers in the margin indicate pagination in the foreign text.

were then cast. The cyclodehydration of PAA into the corresponding polyamides was carried out at 200-230° in vacuo (approximately 10^{-2} mm). In order to preserve film strength, the additives were introduced in a molar ratio of 1:20 with respect to polymer segments, although homogeneous films can be made at ratios of 1:5 or higher. It was shown that in the cases when infrared absorption of the additive in the film (TCQM) can be observed, the cyclodehydration of the PAA does not lead to significant changes in the additive concentration.

Spectra recorded from the difference in absorption of the polyimide films with and without an acceptor are characterized with a wide band in the visible spectral region, indicating the formation of charge transfer complexes. Thus, for example, the absorption bands of the charge transfer complexes of p-chloranil with polypyromellitimide based on 4,4'-diaminodiphenylamine ($\lambda_{max} \simeq 540$ nm), with the model compound N-(4-diphenylamino)phthalimide (590 nm), and with diphenylamine (650 nm) are similar in shape, but the shift of the maximum of absorption into the series diphenylamine > model > polyimide is apparently associated with the influence of the electron-acceptor imide substituents. The absorption of charge transfer complexes in polypyromellitimides is masked by the intense absorption of the polymers proper in the visible spectral region and it can be revealed only by recording the difference spectra. In polyimides based on DODA or DSDA, the intrinsic absorption of the polymers is weaker and is shifted toward the shorter wavelength direction, owing to which the bands of the charge transfer complexes show up distinctly in spectra measured with respect to air. Typical spectra are presented in Fig. 1 for the case of the charge transfer complex of a polyimide of DODA and 4,4'-diamino-N-methyldiphenylamine with p-chloranil, with o-bromanil, with TCQM and DCDC. As can be seen from the data in the table, the diphenyl compounds, when inserted into the polyimide chain, mainly retain their electron donor character.

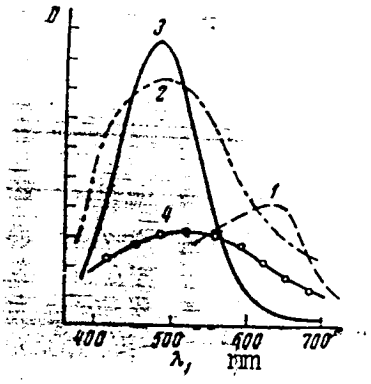


Fig. 1. Absorption spectra of charge transfer complex of polyimide based on 4,4'-diamino-N-methyldiphenylamine and DODA with p-chloranil (1), o-bromanil (2), TCQM (3), and DCDC (4)

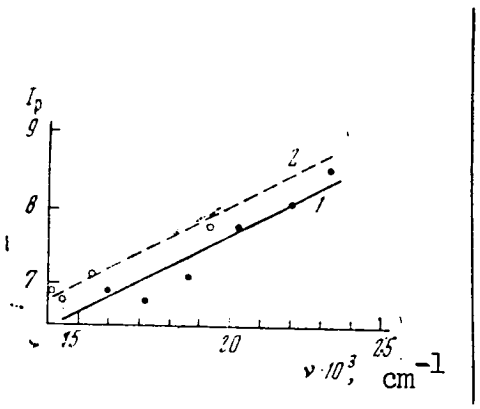


Fig. 2. Absorption maxima of charge transfer complex of p-chloranil with polyimides (1) and with the corresponding diphenyl compounds (2) as a function of the ionization potentials of the latter

Shown in Fig. 2 are the absorption maxima of charge transfer complexes of polypyromellitimides (line 1) and the corresponding diphenyl compounds (line 2) with p-chloranil with respect to the ionization potentials of the diphenyl compounds[1]. The resulting functions can be represented with straight lines extending in parallel, which indicates an approximately identical (by approximately 0.3 eV) in the ionization potential of the donor compounds when introduced into the polyimide chain. The maxima of the polyimide charge transfer complexes show practically no shift when the dianhydride residue is modified, as can be seen in the case of polyimides based on 4,4'-diaminotriphenylamine and different dianhydrides (Table).

For charge transfer complexes of diphenyl compounds (diphenylamine, diphenyl ester, and so on), the presence of two bands with several acceptors (TCE, DCDC) is typical; this is accounted for

[1] The first adiabatic ionization potentials, determined by V.K. Potapov et al, were used.

ABSORPTION MAXIMA OF CHARGE TRANSFER COMPLEXES OF p-CHLORANIL WITH DIPHENYL COMPOUNDS AND WITH POLYIMIDES CONTAINING ANALOGOUS GROUPS IN THE DIAMINE RESIDUE

X	Compound or Polymer	λ_{max} nm
NH	Diphenyl	650
	Polypyromellitimide	540
NCH_3	N-Methyldiphenylamine	700
	Polypyromellitimide	630
	Polyimide based on DODA	640
NC_6H_5	Triphenylamine	700
	Polypyromellitimide	580
	Polyimide based on DODA	580
NC_6H_5	Polyimide based on BPDA	565
	Polyimide based on DSDA	585
	Polyterephthalimide	635
S	Diphenylsulfide	520
	Polypyromellitimide	495
O	Diphenyl ester	450
	Polypyromellitimide	450
CH_2	Polypyromellitimide	430

by the participation in the donor-acceptor interaction, of two types of orbitals in the donor molecule. The position and intensity of the long-wave band, related to the orbital encompassed by a heteroatom, are highly sensitive to displacements in positions 4 and 4'. Possibly associated with this is the absence of long-wave bands in the spectra of charge transfer complexes of the corresponding polyimides with TCE and DCDC. In the case of polyimide films containing TCQM, it was not possible to find any position that could be associated with the charge transfer complex. The intense band observed in the region 400-500 nm is probably related to the displaced position of the acceptor per se. This kind of long-wave shift in the absorption maximum of an acceptor was observed earlier for the charge transfer complex of p-chloranil with certain p-donors [7]. In the spectra of PAA films containing TCQM, absorption of the anion-radicals TCQM was observed, disappearing after cyclodehydration. The anion-radicals are also formed in the reaction of diphenylamine and triphenylamine with TCQM in their solution in dichlorethane.

The coloration of polypyromellitimides successively deepens as the ionization potential of the corresponding diphenyl compound is reduced (from light-yellow in the case of X=CH_2 to dark-red in the case of X=NH or NC_6H_5). If the provisional "absorption edges" (that is, the wave numbers at which the same reduced optical density on the long-wave side of the spectrum is observed) are plotted on a graph versus the ionization potentials of the corresponding diphenyl compounds, a function results that is in agreement with the lines in Fig. 2. Replacing the PDA in the polyimides with the less electron acceptor oriented DODA leads to an abrupt shift in the "absorption edge" in the long-wave direction. Depending on the dianhydride used, the "absorption edge" wavelength of the polyimides changes as follows: DODA < DSDA < BPDA $\simeq$ PDA, which evidently corresponds to an increase in the electron affinity of the anhydrides and, probably, the corresponding diimides. These data are grounds for assuming that the coloration of aromatic polyimides is due to donor-acceptor interaction between the electron-donor residue diamine and the electron-acceptor imide group in the neighboring macromolecules. It is known [8] that aromatic imides form charge transfer complexes with electron donors. It can be assumed that the imide groups inserted into the polymeric chain retain their electron-donor ability.

In a study [9], the coloration of polyimides was related to conjugation in the polymer chain; however, conjugation can hardly be realized between segments in the polyimide chain. The polyheteroarylenes (polybenzimidazoles, polybenzoxazoles), in which conjugation between segments is more probable than polypyromellitimides, are colored less strongly than the latter. Although the coloration of polyimides also depends on the purity of the original compounds, especially in the case of diamines, and on the heat treatment conditions, the main factor determining the coloration is donor-acceptor interaction between macromolecules. However, for a conclusive confirmation of this assumption, it is necessary to spectroscopically study charge transfer complexes of the model compounds

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(pyromellitimide and others) and to compare the results with the corresponding data for polymers.

Conclusions

By electron spectroscopy it was shown that aromatic polyimides containing electron-donor residues of diamines $-C_6H_4-X-C_6H_4-$ ($X = NH$, NCH_3, NC_6H_5, O, S, and CH_2) form charge transfer complexes with low-molecular-weight electron acceptors. Based on the data obtained, the hypothesis was advanced that the coloration of the polyimides per se is due to the formation of charge transfer complexes between the electron-acceptor imide fragments and the electron-donor residues of the diamines.

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